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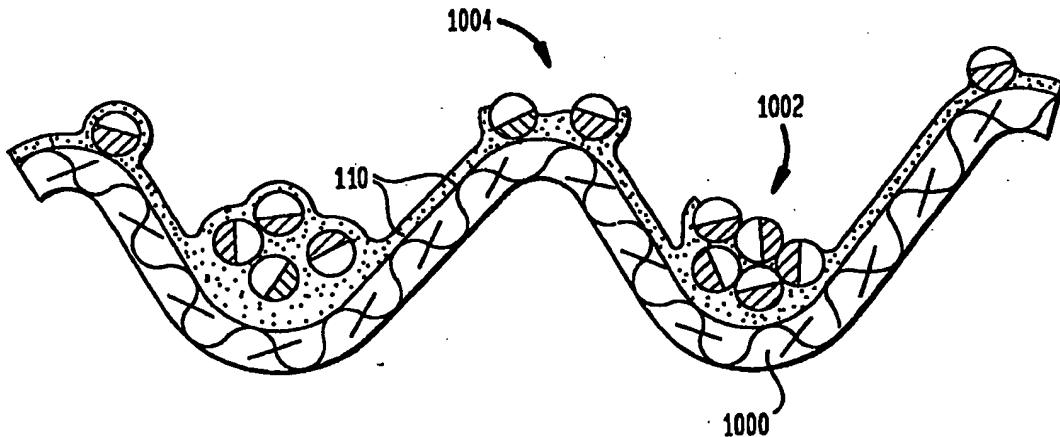
(57) Abstract

A retroreflective composition of the present invention comprises nonvolatile matrix material, an optional volatile constituent, and a plurality of retroreflective microsphere beads and pigment wherein the ratio of the volume of matrix material to the volume of retroreflective microsphere beads plus pigment is in the range of 0 % to 10,000 %, and is optimally suitable for use on fabrics.

RETROREFLECTIVE COMPOSITION

Background of the Invention

Field of the Invention

The present invention relates generally to a retroreflective composition and, more particularly, to a retroreflective composition containing non-volatile matrix material and a plurality of retroreflective microsphere beads.

Related Art

There has been a continuing need for fabrics and other substrates which are inconspicuous during the daytime and reflective at night. One desirable method for achieving these characteristics has been to coat the substrate with a retroreflective composition. Conventional retroreflective coating compositions are disclosed in, for example, U.S. Patent No. 2,963,378 to Palmquist *et al.*; U.S. Patent Nos. 3,099,637, 3,228,897, 3,420,597 and 3,251,704 to Nellessen; U.S. Patent No. 3,535,019 to Longlet *et al.* ; U.S. Patent Nos. 4,103,060, Re. 30,892 and 4,263,345 to Bingham; and U.S. Patent No. 4,187,332 to Fouche Jr.

These conventional approaches have yielded retroreflective substrates having limited practical use for many applications. For example, with respect to garments and other fabrics, these conventional treatments are conspicuous in daytime and have not provided other important qualities such as hand comfort, breathability comfort and daytime colored appearance. Furthermore, although these conventional compositions reflect light, they do not reflect a substantial portion of the light and, therefore, do not provide a brilliant reflection of the light at nighttime. In addition, existing commercial reflective treatments for fabrics often do not wash well under normal conditions and do not pass industry crock standards.

What is needed, therefore, is a retroreflective composition which can brilliantly reflect light at nighttime while remaining inconspicuous in daytime. In addition, the retroreflective composition should have hand comfort, breathability comfort and be capable of providing for daytime colored appearance. In addition, the retroreflective coating should wash well under normal conditions and pass appropriate industry standards.

Summary of The Invention

The present invention is a retroreflective composition that overcomes the above and other drawbacks and deficiencies of conventional compositions, and a method for manufacturing the same. In one aspect of the invention, a retroreflective composition for application to a substrate is disclosed. The retroreflective composition includes a nonvolatile matrix material having a volume and a weight; a volatile constituent; a volume of retroreflective microsphere beads; and a volume of pigment particles having a dimension of not greater than 2 microns. The quantity of pigment particles is sufficient to enable the substrate to reflect color from the pigment particles under daytime conditions. A preferred ratio of the volume of the matrix material to the sum of the volume of the microsphere beads and the volume of the pigment particles is in the range of 0% to 10,000%. Another preferred range for the ratio of the volume of the matrix material to the sum of the volume of the retroreflective microsphere beads and the volume of the pigment particles is approximately 100% to 200%.

In one embodiment, the retroreflective composition also includes an adhesion promoter coating the retroreflective microsphere beads. The adhesion promoter preferably has weight of between .05% and 1% of the microsphere bead weight. In another embodiment, the adhesion promoter has a weight of between .05% and 1% of the weight of the reflective composition.

In another embodiment, upon application of the retroreflective composition to the substrate, the retroreflective composition has a semi-saturated microspheric density of between 20 and 2,000 microspheric beads per square millimeter of substrate.

In another aspect of the invention a substrate having an appearance of being more retroreflective at night when exposed to a beam of light than when exposed to diffuse light is disclosed. Applied on at least a portion of a surface of the substrate is a coating layer that includes a nonvolatile matrix material, a volatile constituent, a plurality of retroreflective microsphere beads, and a quantity of pigment particles having a dimension of not greater than 2 microns. The quantity of pigment particles is sufficient to enable the substrate to reflect color from the pigment particles under daytime conditions and the ratio of the matrix material volume to a volume of the retroreflective microsphere beads plus the pigment particles is in the range of 0% to 10,000%.

In one embodiment of this aspect of the invention, the coating layer also includes a quantity of retroreflective microsphere beads to yield a semi-saturated microspheric density of between 20 and 2,000 per square millimeter of substrate. Preferably, the coating layer is applied to an entire surface of the substrate to form a silhouette when viewed under focused rays of light. In another embodiment, the pigment particles have a diameter/thickness of less than 2 microns. In one embodiment the substrate is a fabric. Preferably, the fabric is configured to form a garment.

In another aspect of the invention a retroreflective composition for application to a substrate is disclosed. The retroreflective composition includes a nonvolatile matrix material having a volume and a weight; a volume of retroreflective microsphere beads; and a volume of pigment particles having a dimension of not greater than 2 microns. The ratio of the volume of the matrix material to the volume of the microsphere beads plus the volume of the pigment particles is in the range of 0% to 10,000%. Preferably, the ratio of the volume of the matrix material to the volume of the retroreflective microsphere beads plus the volume of the pigment particles is approximately between 300% and 800%.

In one embodiment of this aspect of the invention, retroreflective composition also includes an adhesion promoter, having a weight of between .05% and 1% of the microsphere bead weight, coating the retroreflective microsphere beads. In another embodiment, the adhesion promoter has a weight of between .05% and 1% of a weight of the reflective composition.

In another embodiment of this aspect of the invention, upon application of the retroreflective composition to the substrate, the retroreflective composition has a semi-saturated microspheric density of between 20 and 2,000 microspheric beads per square millimeter of substrate.

In still another aspect of the invention, a method for treating a substrate with a retroreflective composition is disclosed. The method includes the steps of: (a) combining a volatile constituent with a non-volatile matrix material to form a coupler compound; (b) adding retroreflective microsphere beads and pigment to the coupler compound to form a retroreflective composition; and (c) applying the retroreflective composition to a substrate. In one embodiment, the substrate is a fabric and wherein the step (c) comprises the step of: (1) applying the retroreflective composition to the fabric using a rotary screen printer. In alternative embodiments, said step (c) comprises the step of: (1) applying the retroreflective

composition to the substrate using any one or more of a flex-o-graphic technique, gravure roll coating technique, blade coating technique, full immersion coating technique and pressurized spray technique. In another embodiment, the method also includes the step of (d) before the step (c), coating the retroreflective microsphere beads with an adhesion promoter.

5   In another embodiment of this aspect of the invention, the method also includes the steps of (d) cross linking said matrix material. In one embodiment, this is performed by heating then cooling the matrix material. In an alternative embodiment, ultra violet lighting is applied to the matrix material. In still another embodiment, the matrix material is exposed to an electronic beam.

10   An advantage of the retroreflective composition of the present invention is that it may be used to form retroreflective substrates which possess daytime appearance, nighttime retroreflectivity, and satisfies industry standards such as the wash, hand, and crock industry standards for texture substrates.

           Another advantage is that the retroreflective composition may include a pigment
15   which will correspond to a color of a substrate or of a desired image, while simultaneously provides brilliant retroreflectivity and attractive daytime appearance.

           A still further advantage of the present invention is that it provides a retroreflective composition which can be either evenly distributed over an entire surface of a substrate or applied in a patterned form or design. In the case of patterned applications, the colored
20   retroreflective composition may be pigmented to impart a desired color.

           A still further advantage of the present invention is that it provides a composition which can be applied to substrates in a solid or patterned form projecting a full reflective silhouette area during nighttime reflectivity. For retroreflective garments, rotary screen printing provides a technologically feasible, commercially viable, and economically efficient
25   means of applying the current-invention to fabric.

           Further features and advantages of the present invention, as well as the structure and operation of various embodiments of the present invention, are described in detail below with reference to the accompanying drawings. In the drawings, like reference numbers indicate like or functionally similar elements. Additionally, the left-most one or two digits of a
30   reference numeral identifies the drawings in which the reference numeral first appears.

Brief Description of The Drawings

This invention is pointed out with particularity in the appended claims. The above and further advantages of this invention may be better understood by referring to the following description when taken in conjunction with the accompanying drawings, in which:

Figure 1 is a cross sectional view of one embodiment of the retroreflective composition of the present invention applied to a substrate;

Figure 2 is a graph depicting the volume ratio between the percent non-volatile matrix material and the percent non-volatile microsphere beads plus pigment particles, referred to as the Matrix Material to Bead+Pigment Volume Concentration, or "MBPVC";

Figure 3 is a table illustrating the density and zero wash reflectivity, dry and wet crock and total volatile volume percent for various MBPVC ratios applied to a Ripstop nylon substrate;

Figure 4 is a photograph of the Ripstop nylon substrate tabularized in Figure 2 having an MBPVC ratio of 20%;

Figure 5 is a photograph of the Ripstop nylon substrate tabularized in Figure 2 having an MBPVC ratio of 100%;

Figure 6 is a photograph of the Ripstop nylon substrate tabularized in Figure 2 having an MBPVC ratio of 200%;

Figure 7 is a photograph of the Ripstop nylon substrate tabularized in Figure 2 having an MBPVC ratio of 400%;

Figure 8 is a photograph of a 100% Cotton T-shirt substrate tabularized in Figure 2 having an MBPVC ratio of 350%, being 100% solid;

Figure 9 is an enlarged cross sectional view of the fabric treated with the composition of the present invention;

Figure 10 is an enlarged cross sectional view of the fabric treated with the composition of the present invention in which multiple layers of microsphere beads have been applied;

Figure 11 is a scanning electron microscope photograph of a fabric illustrated in Figure 10; and

Figure 12 is a table illustrating an exemplary retroreflective composition of the present invention.

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Detailed Description

Figure 1 is a cross-sectional view of one embodiment of the retroreflective composition of the present invention applied to a substrate. The retroreflective composition 100 includes a matrix material 102 securing a plurality of microsphere beads 104A-104D
5   (collectively and generally referred to as microsphere beads 104) to a substrate 106. The microsphere beads 104 are coated with a retroreflective material 108 and are typically completely or partially embedded within the matrix material 102. The substrate 106 is a base material to which the retroreflective composition 100 may be applied. Examples of substrate 106 include, for example, textiles, fabric (wovens, non-wovens, knits etc.), paper, leather,
10   plastic, glass, metals, wood, rubber, synthetic rubber, composites, concrete, asphalt, trees and other materials.

The matrix material 102 is preferably a substantially transparent or translucent non-volatile film-forming resin. The matrix material 102 serves to bind pigment particles 110 and microsphere beads 102 to the substrate 106. In embodiments wherein the substrate 106 is a
15   textile, the matrix material 102 may include, but not be limited to, acrylic, PVC, urethane polymers or unsaturated monomers, such as vinyl chloride, dichloroethene, acrylic acid, methacrylic acid, acrylamide, acrylonitrile, acrylic acid esters, vinyl ethers and vinyl esters, styrene and diolefins, like butadiene, or any combination thereof. In embodiments wherein the substrate 106 is something other than a textile, the matrix material 102 may also include
20   but not be limited to, oils, resins, epoxy, solvents or any combination thereof. In alternative embodiments the matrix material 102 may be any well known resin or emulsion appropriate to bind the pigment particles 110 and beads 104 to the selected type of substrate 106. For example, for other applications such as ultra violet (UV), electronic beam, thermoplastic, thermoset and plastisols (plasticized PVC), the matrix material 102 is the chemical ingredient
25   which binds the pigment particles 110 and microsphere beads 104 to a substrate 106.

The matrix material 102 forms a matrix material layer 112 on the substrate 106. The matrix material layer 112 is the layer of matrix material 102 which, upon treatment of a substrate 106, forms on a surface of the substrate 106 as a result of either the evaporation of the volatile constituent from the non-volatile constituents and/or the curing/setting of the
30   matrix material 102 as a result of elevated temperature, ultra violet light, electronic beam or suitable alternative. This combination of constituents is generally referred to as coupler compound. In addition to the non-volatile matrix material 102, the coupler compound may

also include any necessary additional ingredients to facilitate application to a substrate 106. For example, the coupler compound may include a dispersant, thickener, defoamer, fixer, antifoamer, adhesion promoter, volatile constituent, plastisizers and fillers, and ammonium hydroxide. The volatile constituent may be any liquid component, if applicable, which is conducive to evaporation.

Upon application to the substrate 106, the matrix material layer 112 preferably has a thickness of less than three-quarters of the diameter of a microsphere beads 104. In a particular embodiment, the matrix material 102 forms a layer 112 between the surface of the substrate 106 and the microsphere bead 104D having a thickness of less than one quarter of the diameter of a microsphere bead 104. This matrix material layer 112 provides a vehicle in which the pigment particles 110 are maintained, and provides both a layer into which the retroreflective microsphere beads 104 are embedded and/or a surface by which the retroreflective microsphere beads 104 may be covered. Achieving this matrix material layer 112 is a result of the ratio of matrix material 102 to microsphere beads 104 plus pigment 110, and from properly controlling the application variables (e.g. viscosity of the coupler compound, application speed, application pressure, and the drying/curing process) for a given substrate.

As noted, the composition 100 is retroreflective. Retroreflectivity refers to the reflecting rays of light which are returned in directions proximate to the opposite of the direction of the incident rays. That is, proximate to the originating path of the incident rays. This property is preferably maintained over wide variations of the direction of incident rays. The light-reflective material which coats each of the microsphere beads to enable the microsphere beads to be retroreflective is preferably a metallic flake such as aluminum. However, as one skilled in the relevant art would find apparent, other retroreflective means 108 may be used. For example, in alternative embodiments, the microsphere beads 104 are coated with a non-metallic material such as organic compounds. Other non-metallic materials such as those described in U.S. Patent No. 3,700,305 to Bingham may also be used. The resulting microsphere beads 104 are referred to herein as retroreflective microsphere beads. In a preferred embodiment, the retroreflective microsphere beads 104 are hemispherically coated; that is, the retroreflective means covers approximately one half of the microsphere bead's surface area. In alternative embodiments, this outer surface may is also colored to improve daytime unnoticability.

The microsphere beads 104 have a preferred diameter in the range of approximately 5 to 500 microns and more preferably 20 to 200 microns. In accordance with one preferred embodiment of the present invention the microsphere beads 104 have an average diameter of approximately 25 to 75 microns. In another preferred embodiment, the diameter of the microsphere beads 104 is approximately 50 microns. In a particular embodiment, the beads 104 are constructed of glass and have a diameter of approximately 50 microns. Empirical studies have shown that at this preferred diameter the microsphere beads 104 have the highest retroreflectivity and daytime unnoticability. It is understood, however, that other diameters which achieve high retroreflectivity and daytime unnoticability are possible. In addition to the myriad of characteristics of the retroreflective composition 100 itself, it is apparent that the type of substrate 106 also bears on the optimum bead size. For example, on fabric substrates if the average bead size exceeds 100 microns, the flexibility, launderability, handling, daytime unnoticability and crock standards begin to degrade.

The hemispherically-coated microsphere beads 104 have a reflective means 108 coated thereon to achieve a desired refractive index for a given application. In one preferred embodiment, the refractive index of retroreflective microsphere beads 104 is approximately in the range of 1.5 to 2.5, subject to the desired use, and may be clear or colored, as well as hollow or solid. In one preferred embodiment, the refractive index is approximately 1.9 to provide efficient retroreflectivity and daytime unnoticability. The 1.9 refractive index provides such retroreflectivity and daytime unnoticability when the retroreflective microsphere beads are 104 viewed under normal dry conditions. In another embodiment, when the retroreflective microsphere beads are covered with plastic or water the optimum value for the refractive index of retroreflective microsphere beads is greater than 2.0, typically in the range of 2.1 to 2.5.

There are many known methods for applying the retroreflective means 108 to the microsphere beads 104. One preferred approach is as follows: A carrier web is first coated with a layer of adhesive in which the microsphere beads 104 are removably embedded in a position adjacent to the surface of the carrier web. The adhesive should be capable of being dissolved or the microsphere beads 104 should be able to be removed from the adhesive at a later stage. The adhesive binder may be applied to the carrier web by screen printer, blade, rod, roller, direct gravure, spray or any method that is suited to laying down a specific quantity of adhesive over a defined area. The adhesive binder is preferably deposited to leave

a thickness of approximately 50% of the diameter of the microsphere beads 104 when the adhesive is dried, and as such the deposit should allow for the evaporation of any solvent content in the adhesive when the drying/curing process takes place.

When the adhesive becomes sufficiently tacky on the carrier web, the microsphere beads 104 are deposited on the tacky web. The microsphere beads 104 are preferably applied over a maximum possible area and are also preferably embedded to approximately half their diameter in the adhesive. The spheres 104 may be distributed over the surface area by any well-known means such as cascading, sifter or aerated hopper onto the tacky adhesive binder. Other techniques are considered to be within the scope of the present invention.

In some embodiments, the carrier web is then passed through pressure rollers to ensure that the retroreflective microsphere beads 104 are securely embedded in the adhesive and are located adjacent to the carrier web surface. The rollers typically also press any loose spheres 104 into any available spaces to insure maximum coverage, to achieve a monolayer of spheres over the total surface area of the carrier web. Excess microspheres may be removed by brushing or suction. The coated carrier web is then passed through an oven or drying/curing facility to activate the adhesive binder and/or to further drive off any solvent content of the adhesive.

The coated carrier web is then passed through a region of a high vacuum deposition chamber wherein a layer of retroreflective means is deposited over the exposed hemispheres of the microsphere beads 104. High vacuum deposition procedures and application methods concerning this process are well known. An aluminum deposit of approximately 50 to 250 Angstroms is sufficient to provide an opaque deposit with good reflecting properties. Alternative means of depositing a layer of retroreflective means are sputtering, electroplating, spraying, heat transfer or coating, all of which are considered to be well-known in the art.

As noted, both retroreflective microsphere beads 104 and pigment particles 110 are applied to the coupler compound to form the retroreflective composition 100 of the present invention. Pigment/dye particles are well-known in the art. As used herein the term pigment particle refers to a colored or non-colored particulate solid which is insoluble in, and essentially physically and chemically unaffected by, the vehicle in which particles are incorporated.

The pigment particles may be numerous colors and may be synthetic, synthetic organic or organic materials. Synthetic materials may include, for example, carbon black,

titanium dioxide of the rotile and anatase types, copper and aluminum alloys, iron oxide, titanium dioxide coated glimmer and others. It should be understood that various factors may be considered in the selection of synthetic pigments, including cost, the fastness properties, and the brilliance and coloring capability.

Organic pigments may include, for example, azoic, carbazole, diarylide, pyrazolone, phthalocyanine, quinacridone, vat, black and white and others. In another embodiment, the pigment particles include reflective pigment particles such as nacreous (pearlescent) or metallic flake in order to achieve fashionable luster-like colors or a traditional reflective (metallic) appearance. Transparent pigment particles, as compared to opaque pigment particles, yield improved retroreflectivity under nighttime conditions. It is understood that other types of pigments may also be used. For example, glow in dark, fluorescent and phosphorescent pigments/dyes may be used to achieve a desired combinational effect, such as fluorescent in daytime and retroreflective in nighttime.

In an alternative embodiment, the pigment particles include reflective pigment particles in combination with untreated glass beads rather than hemispherically reflectorized glass beads. Untreated glass beads in combination with reflective pigment particles such as nacreous or metallic flakes may be used to achieve a desired retroreflectivity. In this embodiment, the glass beads are randomly positioned on top of the nacreous or metallic flakes which evenly coat the substrate. Light rays penetrate the glass beads, reflect off of the nacreous or metallic flakes and return through the glass beads towards the source of the light. In some embodiments the metallic flake is aluminum. In other embodiments, colored metallic flakes are used. Such embodiments are relatively inexpensive to manufacture and achieve similar daytime unnoticability and nighttime retroreflectivity as the above preferred embodiments. It is noted that additional color pigment particles less than 2 microns may be added to achieve daytime unnoticability or fashionable colors as desired.

Various types of pigments are commonly available. In one embodiment of the retroreflective coating 100, synthetic pigments are utilized. Synthetic pigments are commonly available in several grades or size ranges. In the practice of the present invention, the pigment particles preferably have a thickness or diameter of less than 2 microns. In another preferred embodiment, the pigment particles 110 have a thickness/diameter of less than 1 micron. Such pigment/dye particles of less than 1 micron uniformly coat the substrate 106 in a continuous manner. The small size of the pigment/dye particle enables the

pigment/dye to bond directly to the substrate 106. A pigment particle with a thickness/diameter of less than 2 microns, which is substantially smaller than the preferred size of the microsphere beads 104 of the present invention, does not deter retroreflection at nighttime and enhances daytime unnoticability, while providing flexibility, and passing crock,

5   launderability, and crock reflectivity loss industry standards.

The crock standard is a standard established by the American Association of Textile Chemists and Colorists (AATCC) Crockmeter Method used in the industry to measure the amount of colorant which is transferred from the surface of a colored fabric to another surface, principally by rubbing. The percentage of reflectivity lost when the AATCC

10   Crockmeter Method is applied to a substrate is referred to as the crock reflectivity loss. Other standards often not achieved by conventional retroreflective compositions are the laundering standard and the hand standard. The laundering standard is a standard established by the AATCC standardization of Home Laundry Test Conditions which is used in the industry to measure the amount of colorant which is lost as a result of one to twenty (20) wash/dry

15   cycles. The hand standard is a standard established by the AATCC for subjective evaluation of fabric hand test method used in the industry to measure the tactile qualities of a fabric. The tactile qualities of a fabric include the softness, drape, flexibility, firmness, elasticity, fineness, resilience and other qualities perceived by touch.

Specifically, in the embodiment as shown in Figure 1, pigment particles 110 having a

20   dimension size of less than 2 microns enable the pigment particles 110 to flow evenly throughout the entire surface area of the matrix material 102. The pigment particles 110 are enabled to lodge on top of, adjacent to, and beneath retroreflective microsphere beads 104. The advantage of this pigment particle placement is that the daytime unnoticability is enhanced by the uniformity which will necessarily occur upon the application of the

25   retroreflective composition 100 to a substrate 106. Further, in contrast to large pigment particles which attach to fibers in a discrete manner, the pigment particles of the present invention attach to fibers in a continuous fashion. In one embodiment, the matrix material 102 is approximately 150 - 175% of the volume of the pigment particles 110 plus the retroreflective microsphere beads 104. In this embodiment, the less than 2 micron diameter

30   sized pigment particles is sufficiently small as to not interfere with the flexibility, wearability, breathability, and crock, launderability, crock reflectivity loss industry standards, while requiring a small volume of matrix material to adhere them to the substrate. In an alternative

embodiment, the matrix material 102 is approximately 100 - 200%, less than 300%, and greater than 75%, although other ratios are considered to be within the scope of the present invention.

Further, with a pigment particle having a dimension of less than 2 microns, the noted preferred microsphere diameter of approximately 50 microns does not prevent any of the pigment particles 110 from entering and adhering in the matrix material 102. Thus, even if two microsphere beads 104 of 50 microns are adjacent to each other, the pigment particles 110 have sufficient space within which to lodge between the microsphere beads 104, or gather below and/or on the top surface of the microsphere beads 104, to provide sufficient pigment throughout the resulting coated substrate surface.

If the pigment particles 110 have a dimension which is greater that 2 microns, the pigment particles 110 may remain in the matrix material 102 provided there was sufficient room between the microsphere beads 104 to allow the pigment particles 110 to pass through. Alternatively, if the microsphere beads 104 are sufficiently close to each other, the microsphere beads 104 may provide a support surface on which other pigment particles 110 are deposited. However, in the latter case, a pigment particle 110 having a dimension greater than 2 microns will likely interfere at nighttime with a light source from contacting the underlying microsphere bead 104, and also prevent the return of the retroreflective rays. With pigment particles of less than 2 microns, the pigment particles 110 do not adversely interfere with the retroreflective properties taught by this invention.

It should be noted that for a given a volume percent of pigment (4% for instance) the surface area that can be covered is far greater the smaller the pigment size (that is, less than 2 microns). This has significant benefits in that less pigment is required to achieve desired colors. Either additional matrix material or retroreflective microsphere beads may be added in place of the pigment particles to optimize the end use product as desired.

As noted, a volatile constituent may be added to the matrix material 102 in the formation of the coupler compound. This may be done, for example, to minimize the amount of the matrix material 102 on a substrate 106, or to provide increased fluidity of the matrix material 102. Also noted above is the addition of other ingredients to the coupler compound to facilitate application to the substrate 106. The volatile constituent may consume any predetermined volume-percent of the coupler compound, from 0 to 99%. In one embodiment, the volatile constituent is water and comprises approximately 65% volume percent of the

coupler compound of the present invention. In another embodiment, there is no volatile constituent. That is, 100% of the coupler compound is non-volatile.

Upon formation of the coupler compound, the retroreflective microsphere beads 104 are added to the coupler compound to form the retroreflective composition 100 of the present invention. The retroreflective composition 100 is then applied to a substrate 106 and cured. Upon evaporation/curing/heat setting of the coupler constituent, the matrix material 102 forms a matrix material layer 112 into which the retroreflective microsphere beads 104 are embedded and may be covered. As shown in Figure 1, microsphere beads 104 are not all covered with the matrix material layer 102. As noted above, in one embodiment, the matrix material layer 112 has a thickness of less than one quarter of the diameter of a microsphere bead 104 between the surface of the substrate 106 and the microsphere beads 104B and 104C.

As noted, a variety of optional ingredients may be included in the coupler compound to achieve desired results. For example, anti-foaming and defoaming agents may be included in the coupler compound to minimize foaming of the compound as it is being formulated or when it is applied to a substrate. In addition, adhesion promoters may be included in the coupler compound. Adhesion promoters include, but are not limited to, titanates, organofunctional silanes, zirconates, zircoaluminates, alkyl phosphate ester, and chartwell. Examples of silanes include, but are not limited to, gamma-Glycidoxypropyltrimethoxysilane, gamma-Aminopropyltriethoxysilane and gamma-Aminopropyltrimethoxysilane. Further, softeners may be included in the coupler compound. Softeners improve the hand of the fabric by offsetting the harshness of the microsphere beads and pigment matrix film. Examples of softeners include low, medium and high density polyethylene, polydimethylsiloxane mixture, and reactive and elastomeric silicone, as well as emulsions of mineral 0:1.

Further, dispersants may also be included in the coupler compound. Examples of dispersants include, but are not limited to, tymol dispersant, acrylic polymers, and naptholene sulphanates. Thickeners may be included in the coupler compound. Examples of thickeners include, but are not limited to, acrylic polymers, natural gums, hydrocarbons, alginates, and white spirit. Additives to encapsulate or "liquify"/disperse non-volatiles such as Polyvinyl Chloride (PVC), acrylics, methacrylics, etc. are commonly referred to as plastisizers. Plastisizers may include, for example, phthalates, adipates, phosphate esters, diectylphthalate, tricresyl phosphate or cresyl diplenyl phosphate. Reducers/detactifiers are often used to reduce viscosity. Antiwiks, emulsifiers and humectants may be added to improve print and

flow qualities. Fixers may be included in the coupler compound. Examples of fixers include, but are not limited to, methylated melamine formaldehyde, and DMDHEU, trimethoxymethylmelamine (TMMM) and hexamethoxymethylmelamine (HMMM).

In one embodiment of the invention, an adhesion promoter is coated onto the individual corrosion protected retroreflective microsphere beads prior to the inclusion of the retroreflective beads into the coupler compound to form the reflective composition of the present invention. To gain optimal adhesion, the adhesion promoter constitutes between approximately .05% and 1% of the bead weight, depending upon the surface area of the retroreflective microsphere bead. In an alternative embodiment, the adhesion promoter constitutes between approximately .05% and 1% of the weight of the reflective composition.

The relative amounts of the ingredients of the retroreflective composition of the present invention will, of course, vary depending upon the particular ingredients employed, the type of substrate, the substrates intended use, as well as such factors as the specific size and quantity of the retroreflective microsphere beads.

In one embodiment, to achieve one or more of the advantageous properties when coating the substrate 106 with the retroreflective composition 100 of the present invention, it is preferable to maintain a relationship of volume ratios of discrete insoluble particles within the composition 100. This volume ratio is defined herein as being independent of any volatile content (if used) in the composition 100, for it is only the nonvolatile ingredients which remain after evaporation of any volatile ingredients. Further, among the nonvolatile ingredients, only the matrix material 102, the retroreflective microsphere beads 104, and the pigment particles 110 compose the retroreflective composition 100 having the volume ratio identified above. Any other volatile and/or non-volatile components of the composition 100 relate solely to the printing ability and quality of the composition 100 when applied to a particular substrate 106. Thus, the volume ratio described according to the present invention relates solely to the volume of matrix material 102, retroreflective microsphere beads 104 and pigment particles 110.

One volume ratio of significance to the present invention is the ratio of the volume of matrix material 102 to the volume of retroreflective microsphere beads 108 plus pigment particles 110. This ratio, referred to herein as the Matrix-to-Bead+Pigment Volume Concentration ("MBPVC"), is approximately between 0% and 99,000%.

Figure 2 is a graph showing the relationship of the volume percent of matrix material

102 and the volume percent of retroreflective microsphere beads 104 plus pigment particles 110 for a preferred MBPVC ratio range of 0% to 10,000%. The horizontal axis represents the volume percent of non-volatile retroreflective microsphere beads 104 plus pigment particles 110 while the vertical axis represents the volume percent non-volatile matrix material 102.

5   The sum of the matrix material 102, the pigment particles 110, the microsphere beads 104, the volatile constituent and any optional ingredients equal 100% of the retroreflective composition 100.

There are three main regions illustrated in Figure 2, each representing a different general category of retroreflective composition 100 which may be formulated and applied to a

10 substrate 106 to form a coated substrate having characteristics which meet a specific end customer's needs. The illustrated range of the MBPVC ratio results in a coated substrate 106 ranging from those which are highly visible at nighttime (that is, high retroreflectivity) to those which are barely visible at nighttime (that is, low retroreflectivity) but which possess excellent daytime colors and are more likely to be considered to be fashionable. Between

15 these two extremes the coated substrates provide for both high visibility at night and a wide spectrum of fashionable colors while ensuring hand comfort, breathability comfort and passing the industry standards, all of which are described below. The regions of the graph 200 are described in detail below.

Formulations having a MBPVC ratio in region 202 (MBPVC ratio = 0 - 50%) will

20 produce a reflective composition 100 which can be applied to produce a highly visible product owing to the high volume concentration of retroreflective microsphere beads 104. This high concentration may make a fabric substrate 106 less flexible and stiffer. In addition, this concentration may result in difficulty in obtaining bright pigment colors. Retroreflective compositions in this region may be used in the creation of coated substrates for objects for

25 which increasing nighttime visibility is paramount and daytime unnoticability, durability, and hand of the substrate 106 are less important.

Formulations having a MBPVC ratio in region 206 (MBPVC ratio = 185% - 10,000%) will produce a reflective composition 100 which can be applied to produce a highly fashionable but less visible product owing to the lower volume concentration of

30 retroreflective microsphere beads 104. This low concentration improves the substrates daytime unnoticability and allows for the addition of additional matrix material 102 and pigment particles 110 and even reduce the volume of retroreflective microspheres 104. It is

noted, however that as the volume of retroreflective microspheres 104 is reduced and more matrix material 102 is added, the MBPVC ratio rapidly increases. Retroreflective compositions 100 in this region may be used in the creation of products for customers who are highly concerned with increasing daytime unnoticability (fashionability) and less

5   concerned with the nighttime visibility of an object.

Formulations having a MBPVC ratio in region 204 (MBPVC ratio = 51% - 184%) will produce a reflective composition 100 which can be applied to produce a coated substrate which provides a preferred tradeoff between the region 202 and 206. The result in region 204 is a coated substrate in which matrix material 102, pigment particles 110, retroreflective

10   microspheres 104 or other constituents may be added to the retroreflective composition. This enables the retroreflective composition 100 to have any desired properties. For example, the coated substrate may be designed to be more fashionable (more pigment) or more reflective at night depending on the customers desires. This region of ratios is to be used when customers are very concerned with increasing daytime unnoticability (fashionability) and equally

15   concerned with the nighttime visibility of an object.

In addition, percent solid lines 208 and 210 are provided. The percent solid lines illustrate that the relative concentration of volatile constituents is relative to the proximity of the concentration point to the origin of the graph 200. For example, line 210 represents the 100% (non-volatile) solids line or the MBPVC ratios where 100% of the coupler compound

20   volume is solid and there is no volatile portion to the composition. Examples of 100% non-volatile compositions are thermoplastic (PVC dispersions), thermoset, ultraviolet, electronic beam. It should be understood that the optimal MBPVC ratio is not restricted by region, but by the specific gravities of matrix/pigments available in the industry and the desired substrate being coated. Hence, on optimal MBPVC ratio for a plastisol formulation

25   may be, for example, in the range of 300%.

Line 208 represents the 40% volatility line or the 60% non-volatile line (solids). At any point along this line there is 100% volume; 40% volatile, 60% non-volatile which consists of the sum of the matrix material, the pigment particles, and the retroreflective microsphere beads. One may readily see that there are hundreds of lines similar to line 208,

30   one at each complement of the % non-volatiles which the formulator creates.

In one preferred embodiment the MBPVC ratio is approximately 150%. This ratio results in a thin layer of matrix material 102 that does not interfere with a source of light

reaching the back surface of the microsphere beads 104 upon which the retroreflective means 108 is coated. When the layer of matrix material 102 through which light must pass is thick, the light beam will be refracted, thus preventing an adequate retroreflection of the light.

In addition, this preferred embodiment supplies a sufficient amount of matrix material 102 to insure the retroreflective microsphere beads 104 are secured firmly to the substrate 106. When the substrate 106 is a fabric, this preferred range of MBPVC ratio also results in a coated substrate satisfying industry crock, laundering and crock reflectivity loss standards. Also, this prevents the creation of additional extraneous matrix material 102 which results in poor tactile qualities of the substrate, and provides a vehicle in which the pigment particles 110 may be uniformly embedded in the matrix material 102 to provide sufficient pigment particle coverage over the entire surface area of the desired portion of the substrate 106. The entire surface area of a fabric may be treated with the retroreflective composition of the present invention to project a full reflective silhouette and still maintain its original daytime unnoticability and tactile qualities.

In another preferred embodiment, when the retroreflective composition includes a volatile constituent, the MBPVC ratio is approximately between 0% and 400%, and more preferably approximately between 0% and 200% and still more preferably approximately between 100% and 200%. In another preferred embodiment, when the retroreflective composition does not include a volatile constituent, the MBPVC ratio is approximately between 0% and 2000% and more preferably, approximately between 100% and 1000%, and still more preferably, approximately between 200% and 800%. It is understood that other ratios may be preferred depending upon which of the above and other characteristics are desired.

Figure 3 is a table illustrating the results of experiments which were performed on a Ripstop Nylon and a 100% Cotton T-shirt substrates coated with the retroreflective composition 100 of the present invention. In addition, the test results shown in the Table depict the dry and wet crock tests which are provided by the industry. The tests were conducted on a scale of 1 to 5. Figures 4-8 are photographs of the coated substrate associated with each of the MBPVC ratios tabularized in Figure 3.

Five experiments were performed. Experiments 1-4 contained a volatile constituent and were applied to a lightweight Ripstop nylon. Holding both application method and viscosity constant, one sees a correlation between the MBPVC ratio, reflectivity (Ra) and the

density of reflective beads per square millimeter (SQMM). As the MBPVC ratio increases, there is a decrease in the density of reflective beads/SQMM which corresponds to a decreased reflectivity reading on the fabric.

A closer examination of Figures 4-7 reveal the lower the MBPVC ratio (Figure 4,

5   MBPVC ratio = 20%), the higher the density of reflective microsphere beads. In Figure 4, the density is so high (409/SQMM) that the microsphere beads form multi-tiered layers which result in microsphere beads laying on top of other microsphere beads. There are diminishing returns in continuing to coat a substrate with layers upon layers of reflective microspheres as the bottom layer(s) do not readily make contact with light rays allowing them to serve a

10   functional purpose of returning the light rays.

Even at a MBPVC ratio = 100% (Figure 5), the microsphere beads form multi-tiered layers in the lower portions of the woven fabric's surface. At a MBPVC ratio = 200% (Figure 6), very few (if any) microspheres lay on top of another. At a MBPVC = 400% (Figure 7), the density of reflective microspheres/SQMM is sufficiently small (16/SQMM) as to almost

15   ensure a very sparse monolayer of microsphere beads on the fabric.

Note that the lower the MBPVC ratio and the higher the density of reflective microspheres/SQMM, the greater the surface area for diffuse daylight to make contact with a reflective microsphere bead as opposed to a similar surface area covered by only pigment. This results in higher reflectivity and decreased daytime unnoticability. Optimizing both

20   reflectivity and daytime unnoticability is possible by creating a weighted scale and testing end use products formulated at various MBPVC ratios. Optimal MBPVC ratio will depend on end use product (customer specifications), application method, matrix selection for application, rheology and substrate. For lightweight Ripstop nylons used for functional outdoor activities, a MBPVC ratio of between 130% - 180% meets both customer daytime

25   unnoticability/durability needs as providing enhanced visibility at night. For fashion purposes only, the MBPVC ratio may soar as high as 99,000%, allowing for only minute retroreflection and mostly daytime unnoticability.

Experiment 5 was formulated as 100% solids and was applied to a cotton T-shirt. Figure 8 portrays the difference between the substrate in 1-4 (woven) versus a knit in

30   experiment 5. The reflective coating needs to stretch more on a knit than a woven. As the substrate and matrix selected for this product is different from that in experiments 1-4, so is the MBPVC ratio. In the case of 100% solids using a PVC matrix, the MBPVC ratio may

range anywhere from 100% to 1,000%; preferably between 200% and 800% to achieve both suitable reflectivity and customer daytime unnoticability/durability. A MBPVC ratio over 2,000% results in a more fashionable and less functional T-shirt product.

To ensure that fabric substrates which were coated with a sufficient amount of retroreflective composition 100 of the present invention provided enhanced safety, nighttime driving tests were undertaken. These nighttime tests were designed and conducted similar to those undertaken by The American Society for Testing and Materials (ASTM) Committee on High Visibility Materials For Individual Safety, with the goal of determining the reflectivity per garment necessary to enhance motorist awareness of a pedestrian.

Reflective fabrics are assessed using four important criteria identified by the ASTM for enhanced visibility. These four criteria include: detectability, conspicuity, recognizability, and localizability. Detectability refers to the characteristic of an object that determines the likelihood that the object will be visible to an observer. For example, when a driver is approaching a sign, the sign will become detectable when the driver's eyes are first capable of seeing it. However, at this point the driver may not have noticed the sign and will not have registered that he is viewing it.

Conspicuity refers to the characteristic of an object that determines the likelihood that the object will come to the attention of the observer. Since one's eyes continuously detect millions of objects, conspicuity implies that the mind has registered the importance of this object and begun to consider it.

Recognizability refers to the characteristic of an object that determines the likelihood that the object will be recognized by an observer. Upon recognition of an object, the motorist can determine whether it is worthy of potential action by identifying whether the object is a sign, another automobile, a person, an animal, or something else.

Localizability refers to the characteristic of an object that determines the likelihood an observer will be able to determine the object's location. Localizability enables a driver to judge the size and position of the object to determine whether the object appears capable of intersecting with the vehicle's path (by mentally judging the closing rate, necessary deceleration, and lateral offset).

These criteria are based on the physiological visual responses that a driver requires to perceive and respond to a potential hazard. Thus, the process by which the eye, brain, and body react to a potentially hazardous situation can be characterized through the four

-20-

previously mentioned criteria. It is important to recognize that unlike garments using traditional retroreflective strips, a garment that reflects a full silhouette provides additional conspicuity, recognizability, and localizability.

A reflectivity number referred to as the Reflectivity per End Use Product (Reup) was
5   measured. This number represents the retroreflectivity of a specific end use product, such as a garment. Reup is a calculated by multiplying the average retroreflectivity reading of the reflective material (Ra) by the number of square meters of reflective fabric used on the garment; the units of this number are candelas per lux per end use product. To calculate the reflectivity per garment (candelas per lux per garment), the retroreflectivity per area of the
10   fabric is measured per ASTM standard E810 using a reflectometer (reflectivity hereinafter referred to as Ra; units are in Candelas per Lux per square meter). Reflectivity per area (Ra) is a ratio that represents the degree of retroreflectivity of a substrate upon which retroreflective microsphere beads are deposited. The Ra is dependent upon the angle between the light source, the substrate and the observer. To obtain a silhouette image it is preferable
15   that a reflective fabric surround a substantial portion of the garment in such a manner to present a visible readily recognizable covered object, such as a human form.

The number of retroreflective microsphere beads per unit of area that are deposited on the substrate to yield daytime unnoticability and nighttime retroreflectivity of the resulting substrate is referred to as the semi-saturated microspheric density. The highest density of
20   microsphere beads that can be attained in a given one dimensional space is 90.69%. The actual number of microsphere beads 104 in a one dimensional space depends on the diameter of the microsphere beads. The optimum microsphere size to achieve the highest retroreflectivity and daytime unnoticability, and for obtaining optimum coatability, dispersion and suspension in the matrix material is approximately 50 microns in diameter. A micron is a
25   thousandth of a millimeter. At 50 microns, the maximum number of microspheres which may be deposited in a matrix material layer is approximately 46,000 microsphere beads per square centimeter or 460 microsphere beads per square millimeter.

In order to achieve these densities the microsphere beads may be deposited in either a multi-tier or monolayer. In either case, the microsphere beads are typically deposited in a
30   randomly oriented manner. That is, when retroreflective microsphere beads are applied to a substrate, they randomly orient themselves with respect to the plane of its surface, providing for retroreflection at a wider range of angles. The greater the orientation of each reflective

bead, the higher the Ra and less volume is required to obtain the same Ra. Figure 9 is an enlarged cross sectional view of a fabric substrate treated with a mono-layer of the retroreflective composition 100 of the present invention, while Figure 10 is an enlarged cross sectional view of the same fabric treated with the composition of the present invention in which multiple layers of microsphere beads have been applied. Figure 11 is a scanning electron microscope photograph of a fabric illustrated in Figure 10.

As shown in Figure 10, with pigment particles 110 less than 2 microns in thickness, the pigment particles 110 provide continuous coverage throughout the entire surface of the fabric 300 regardless of the indentations and ridges inherent in the fabric substrate 300 due to its construction. The retroreflective composition 100 may be applied to such a fabric over its entire surface or in a pattern form. By applying the retroreflective composition 100 to a continuous bolt of fabric 300, the fabric 300 can then be cut and sewn into a garment. Articles of clothing which may be coated with the retroreflective composition 100 of the present invention include, but are not limited to, socks, sneakers, shoes, shoelaces, boots, pants, shorts, shirts, coats, hats, belts, scarves, gloves, packs, bags, daypacks, animal outfits, safety gear, etc. In some embodiments, the fabric on which the retroreflective composition 100 is applied includes, but is not limited to, nylon, cotton, polyester, lycra, fleece, non-wovens, leather, and synthetics.

Referring to Figure 10, multi-tiered microsphere beads 104 refers to the structure of microsphere beads having more than one monolayer of microspheres in portions of the substrate. Specifically, when a substantial number of microsphere beads are deposited onto a square millimeter of the substrate, a portion of the microsphere beads tend to gather on the upper surfaces of the lower-lodged microsphere beads. The beads subsequently group together to form multiple layers, and are referred to as multi-tiered microsphere beads. As shown in Figure 10, a fabric 1000 does not provide a flat surface by which a light ray will be reflected, but rather has indentations 1002 and ridges 1004 due to its construction. Fabric 1000 may be, for example, a weave or knit. As shown in Figure 10, a substantial number of microsphere beads are lodged into the arbitrarily-arranged recesses of the fabric forming a multi-tiered structure. In contrast, a monolayer is created when the microsphere beads are deposited and fail to gather on both the upper and lower surfaces of the substrate. Rather, the beads primarily gather on one surface.

An exemplary coated fabric substrate with a retroreflective composition that when

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applied to the fabric results in a multi-tiered structure of microsphere beads is shown in Figure 11. A discussion of the features and advantages of such an embodiment of the present invention is further described in commonly owned co-pending U.S. Patent Application Serial No. 08/346,887, herein incorporated by reference in its entirety.

5   The present invention will be further described with the following non-limiting example shown in Figure 12. A slurry was prepared from the ingredients shown in Figure 12. The first seven identified ingredients were mixed together for 15 minutes with a high speed mixing blade. After mixing to homogeneity, retroreflective microsphere beads were added and mixed for 5 minutes until uniformly blended. The retroreflective composition is then

10   applied as a single component onto a fabric using a rotary screen printer directly against the fabric resulting in a retroreflective fabric coated with between 20 to 2,000 randomly oriented microsphere beads per square millimeter fabric. Following the application of the particles to a fabric, the composition was dried by forced air heated between 100°F to 250°F for approximately 1-3 minutes and then cured at approximately 350°F for 2 minutes. As a result,

15   the volume ratio of the matrix material to the retroreflective microsphere beads plus pigment is approximately 200%.

Compositions of the present invention can be applied to fabric using conventional textile printing and finishing equipment. Typical methods for flexible substrates include rotary screen printing, rotogravure cylinder, blade over roll, flex-o-graphic, bathing, spraying,

20   and flat bed printing. The typical commercial finishes such as softeners, waterproofing, and water repellency may be applied over the printed composition of the present invention without affecting the retroreflective composition's daytime unnoticability or nighttime reflectivity. For more rigid substances, spraying and painting and roller coating are preferred.

While the invention has been particularly shown and described with reference to

25   particular embodiments thereof, it will be understood by those skilled in the art that the foregoing and other changes in form and details may be made therein without departing from the spirit and scope of the invention.

Having thus described our invention, what we claim as new and desire to secure by Letters Patent is:

30

CLAIMS

1. 1.   A retroreflective composition for application to a substrate comprising:

2   a nonvolatile matrix material having a volume and a weight;

3   a volatile constituent;

4   a volume of retroreflective microsphere beads having a weight; and

5   a volume of pigment particles having a dimension of not greater than 2 microns; said

6   quantity of pigment particles being sufficient to enable the substrate to reflect color from said

7   pigment particles under daytime conditions;

8   wherein a ratio of said volume of said nonvolatile matrix material to a sum of said

9   volume of said microsphere beads and said volume of said pigment particles is in a range of

10   approximately 0% to 10,000%.

1. 2.   The retroreflective composition of claim 1, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of said microsphere

3   bead weight, coating said retroreflective microsphere beads.

1. 3.   The retroreflective composition of claim 1, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of a weight of said

3   reflective composition.

1. 4.   The retroreflective composition of claim 1, wherein upon application of said

2   retroreflective composition to the substrate, said retroreflective composition has a semi-

3   saturated microspheric density of between 20 and 2,000 microspheric beads per square

4   millimeter of substrate.

1. 5.   The retroreflective composition of claim 4, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of said microsphere

3   bead weight, coating said retroreflective microsphere beads.

1. 6.   The retroreflective composition of claim 4, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of a weight of said

3   reflective composition.

1   7.   The retroreflective composition of claim 1, wherein said ratio of said volume of said

2   nonvolatile matrix material to said sum of said volume of said retroreflective microsphere

3   beads plus said volume of said pigment particles is in a range of approximately 100% to

4   200%.

1   8.   A substrate which has the appearance of being more retroreflective at night when

2   exposed to a beam of light than when exposed to diffuse light, the substrate having applied on

3   at least a portion of a surface thereof a coating layer, said coating layer comprising:

4   a nonvolatile matrix material;

5   a plurality of retroreflective microsphere beads; and

6   a quantity of pigment particles having a dimension of not greater than 2 microns; said

7   quantity of pigment particles being sufficient to enable the substrate to reflect color from the

8   pigment particles under daytime conditions;

9   wherein a ratio of a volume of said matrix material to a volume of said retroreflective

10   microsphere beads plus said pigment particles is in the range of 0% to 10,000%.

1   9.   The substrate of claim 8, wherein said coating layer further comprises:

2   a quantity of retroreflective microsphere beads to yield a semi-saturated microspheric

3   density of between 20 and 2,000 per square millimeter of substrate.

1   10.   The substrate of claim 8, wherein said substrate is a fabric.

1   11.   The substrate of claim 10, wherein said fabric is configured to form a garment.

1   12.   The substrate of claim 8, wherein said coating layer is applied to a surface of said

2   substrate to form a silhouette when viewed under focused rays of light.

1   13.   The substrate of claim 12, wherein said coating layer is applied as a pattern on said

2   surface of said substrate.

1 14.   The substrate of claim 12, wherein said coating layer is applied as a substantially

2 complete coating on said surface of said substrate.

1 15.   A retroreflective composition for application to a substrate comprising:

2   a nonvolatile matrix material having a volume and a weight;

3   a volume of retroreflective microsphere beads; and

4   a volume of pigment particles having a dimension of not greater than 2 microns;

5 wherein a ratio of said volume of said matrix material to a sum of said volume of said

6 microsphere beads and said volume of said pigment particles is in the range of 0% to

7 10,000%.

1 16.   The retroreflective composition of claim 15, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of said microsphere

3 bead weight, coating said retroreflective microsphere beads.

1 17.   The retroreflective composition of claim 15, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of a weight of said

3 reflective composition.

1 18.   The retroreflective composition of claim 15, wherein upon application of said

2 retroreflective composition to the substrate, said retroreflective composition has a semi-

3 saturated microspheric density of between 20 and 2,000 microspheric beads per square

4 millimeter of substrate.

1 19.   The retroreflective composition of claim 15, wherein said ratio of said volume of said

2 matrix material to said volume of said retroreflective microsphere beads plus said volume of

3 said pigment particles is approximately between 200 to 800%.

1 20.   A method for treating a substrate with a retroreflective composition comprising the

2 steps of:

3   (a)   creating a coupler compound;

4   (b)   adding retroreflective microsphere beads and pigment to said coupler

5 compound to form a retroreflective composition; and

6   (c)   applying said retroreflective composition to a substrate.

1   21.   The method of claim 20, wherein said step (a) comprises the steps of:

2   (1)   combining a volatile constituent with a nonvolatile matrix material to form a

3 coupler compound.

1   22.   The method of claim 20, wherein said step (a) comprises the step of:

2   (1)   combining a plastisizer with a non-volatile matrix material to form a coupler

3 compound.

1   23.   The method of claim 20, wherein said substrate is a fabric and wherein said step (c)

2 comprises the step of:

3   (1)   applying said retroreflective composition to the fabric using a rotary screen

4 printer.

1   24.   The method of claim 20, wherein said substrate is a fabric and wherein said step (c)

2 comprises the step of:

3   (1)   applying said retroreflective composition to the fabric using a flex-o-graphic

4 technique.

1   25.   The method of claim 20, wherein said substrate is a fabric and wherein said step (c)

2 comprises the step of:

3   (1)   applying said retroreflective composition to the fabric using a gravure roll

4 coating technique.

1   26.   The method of claim 20, wherein said substrate is a fabric and wherein said step (c)

2 comprises the step of:

3   (1)   applying said retroreflective composition to the fabric using a blade coating

4 technique.

1   27.   The method of claim 20, wherein said substrate is a non-flexible substrate and wherein

2   said step (c) comprises the step of:

3   (1)   applying said retroreflective composition to the substrate using a spray coating

4   technique.

1   28.   The method of claim 20, further comprising the step of:

2   (d)   before said step (c), coating said retroreflective microsphere beads with an

3   adhesion promoter.

1   29.   The method of claim 20, further comprising the steps of:

2   (d)   cross linking said matrix material.

1   30.   The method of claim 30, wherein said step (d) comprises the step of:

2   (1) heating then cooling said matrix material.

1   31.   The method of claim 30, wherein said step (d) comprises the step of:

2   (1)   applying ultra violet lighting to said matrix material.

1   32.   The method of claim 30, wherein said step (d) comprises the step of:

2   (1)   exposing said matrix material to an electronic beam.

1   33.   A retroreflective composition for application to a substrate comprising:

2   a nonvolatile matrix material having a volume and a weight;

3   a volatile constituent;

4   a volume of glass beads; and

5   a volume of pigment particles having a dimension of not greater than 2 microns, said

6   pigment particles including reflective pigment particles;

7   wherein a ratio of said volume of said nonvolatile matrix material to a sum of said

8   volume of said microsphere beads and said volume of said pigment particles is in a range of

9   approximately 0% to 10,000%.

1   34.   The retroreflective composition of claim 33, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of said microsphere

3   bead weight, coating said retroreflective microsphere beads.

1   35.   The retroreflective composition of claim 33, further comprising:

2   an adhesion promoter, having a weight of between .05% and 1% of a weight of said

3   reflective composition.

1   36.   The retroreflective composition of claim 33, wherein upon application of said

2   retroreflective composition to the substrate, said retroreflective composition has a semi-

3   saturated microspheric density of between 20 and 2,000 microspheric beads per square

4   millimeter of substrate.

1   37.   The retroreflective composition of claim 33, wherein said ratio of said volume of said

2   nonvolatile matrix material to said sum of said volume of said retroreflective microsphere

3   beads plus said volume of said pigment particles is in a range of approximately 100% to

4   200%.

1/11

## FIG. 1

FIG. 2

% NON-VOLATILE MATRIX

% NON-VOLATILE RETROREFLECTIVE MICROSPHERE
BEADS & PIGMENT PARTICLES
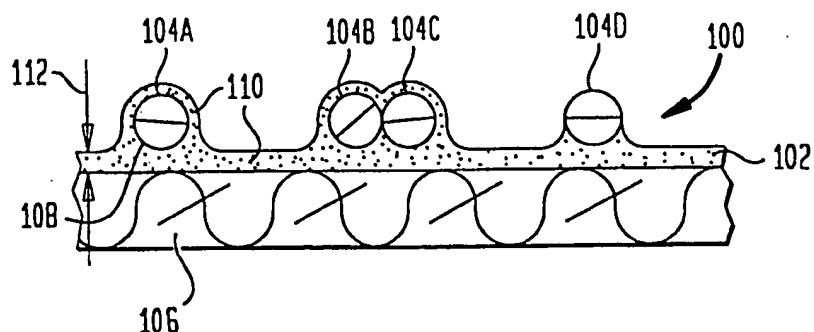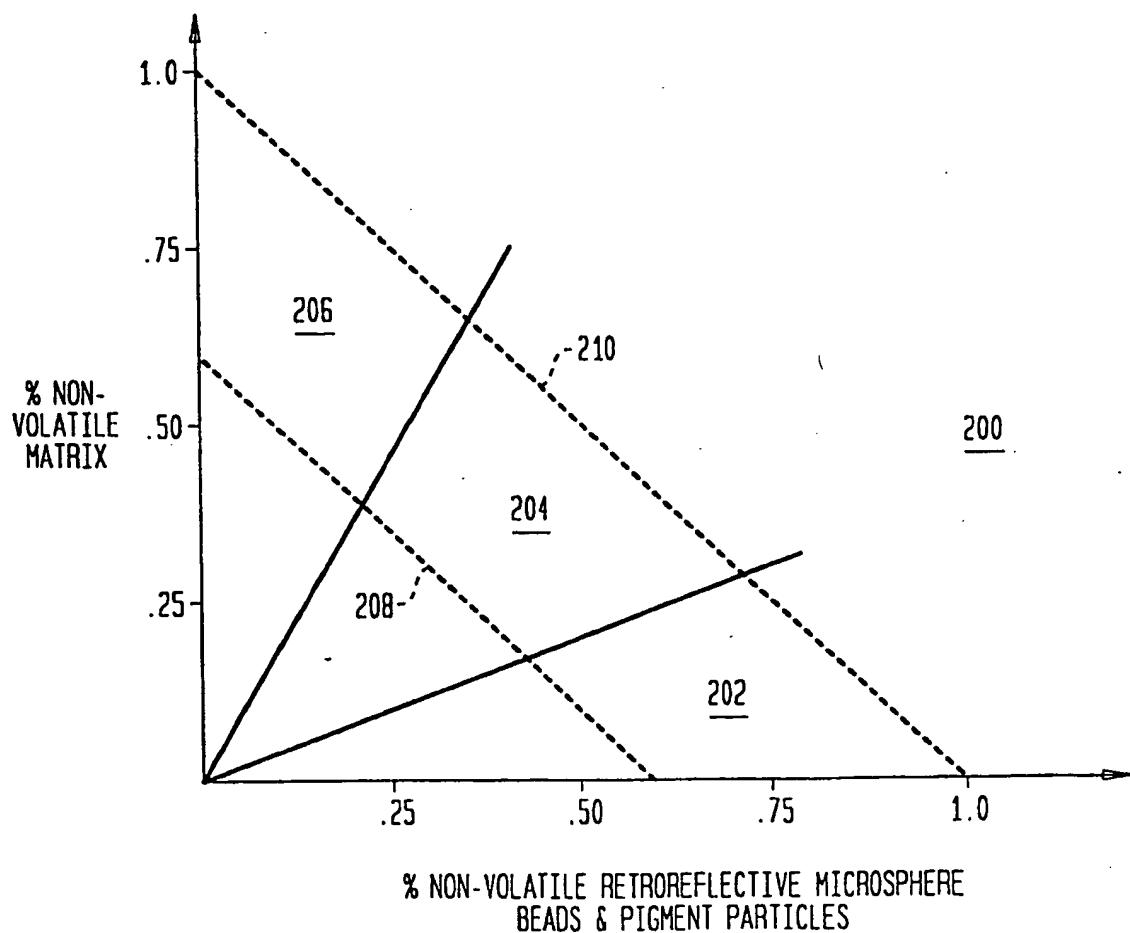
2/11

FIG. 3

EXEMPLARY MBPVC RATIOS						
SUBSTRATE	MBPVC RATIO	DENSITY OF SD/SOMM	ZERO WASH REFLECTIVITY	DRY CROCK	WET CROCK	TOTAL VOLATILE VOLUME %
RIPSTOP NYLON	20%	409	32.5	2	1	57.0%
RIPSTOP NYLON	100%	107	22.7	2.5	1.5	55.0%
RIPSTOP NYLON	200%	65	10.5	2.5	3	51.0%
RIPSTOP NYLON	400%	16	2.7	2	2	68.0%
100% COTTON T	350%	116	12.0	4	3	0.0%

FIG. 4

FIG. 5

1 mm

1 mm

MBPVC = 100%

FIG. 6

MBPVC =200%

1 mm

1 mm

FIG. 7

MBPVC – 100%

1 mm

1 mm
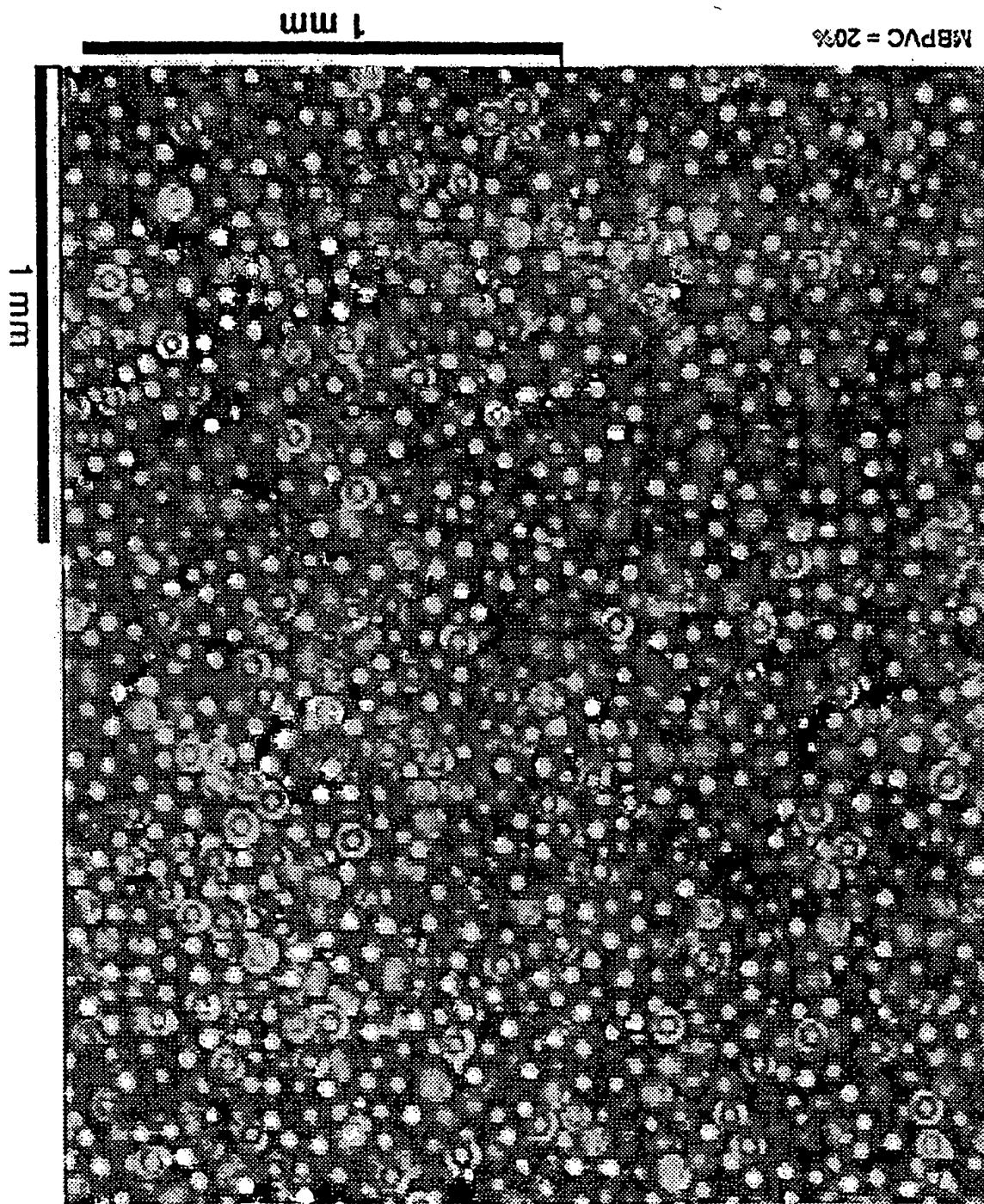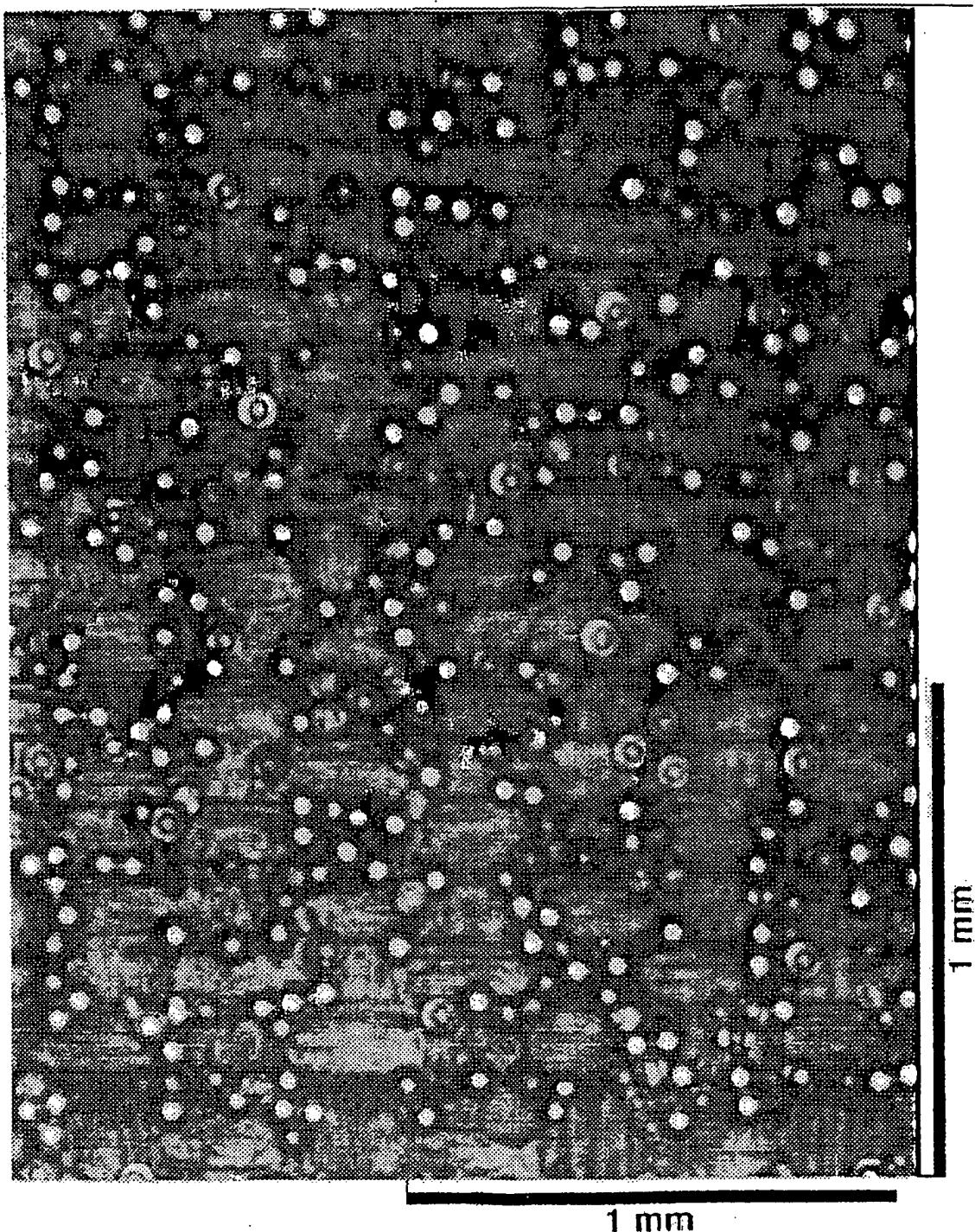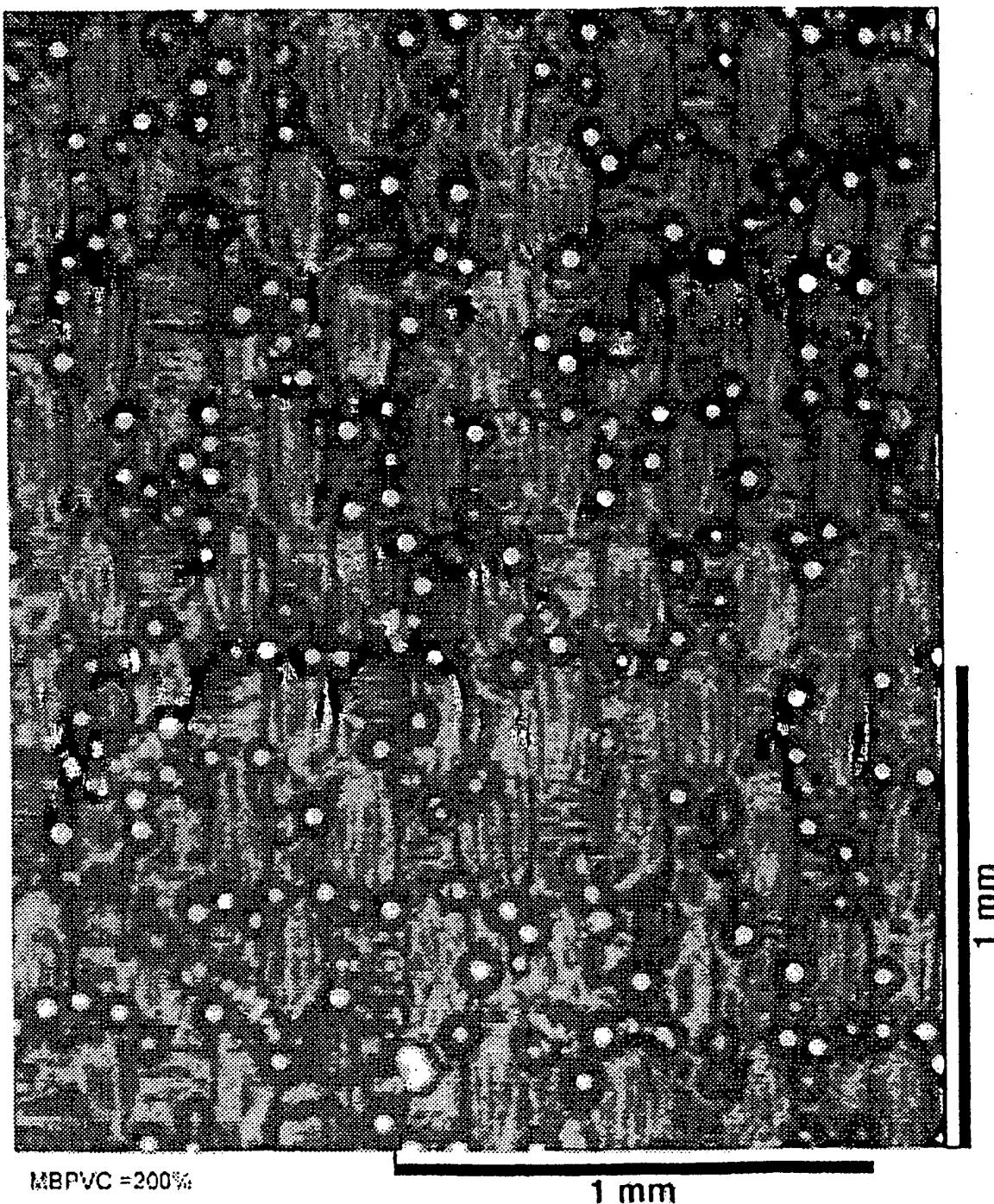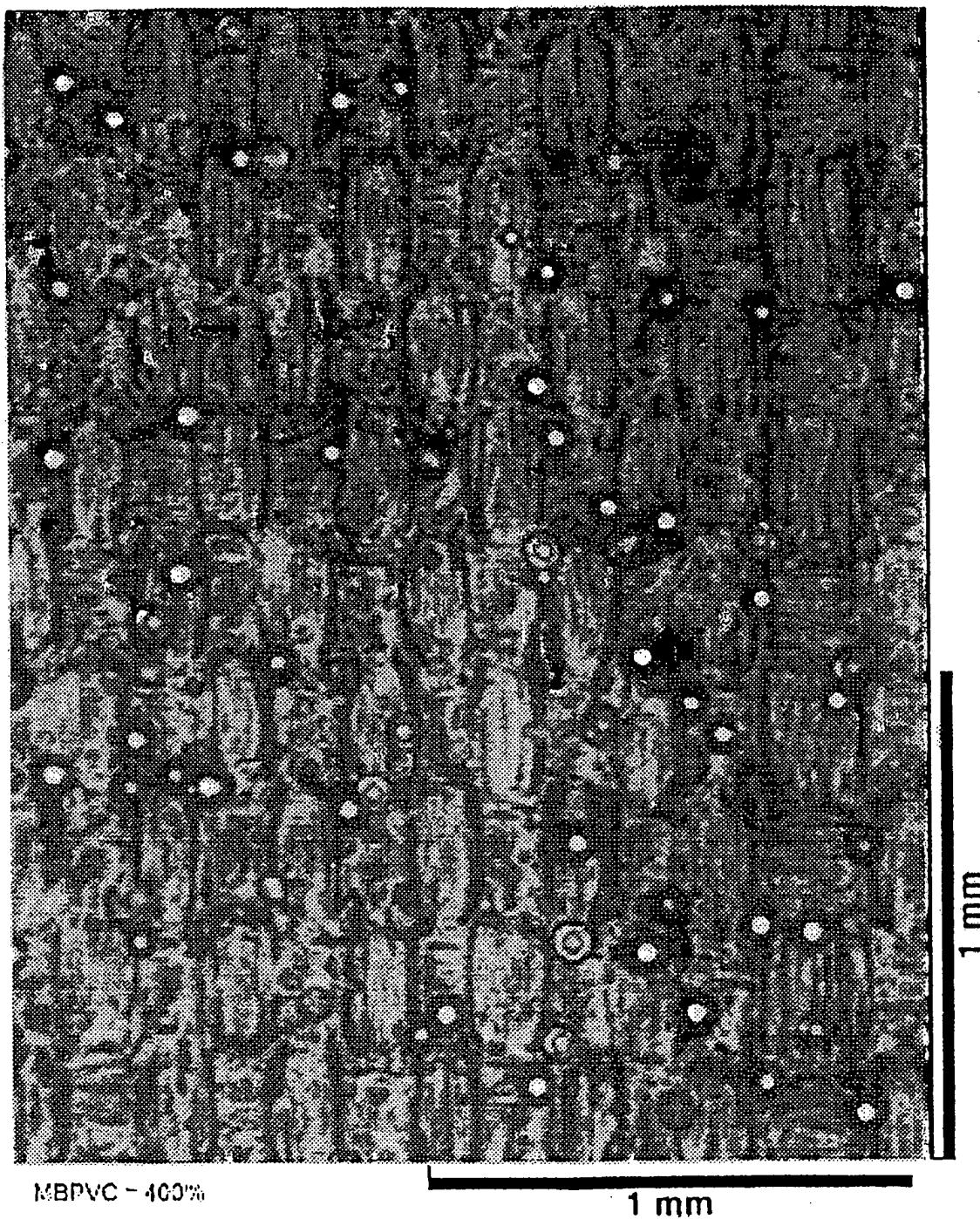
FIG. 8

100% Solid #2

1 mm

1 mm

FIG. 9

FIG. 10

FIG. 11

104
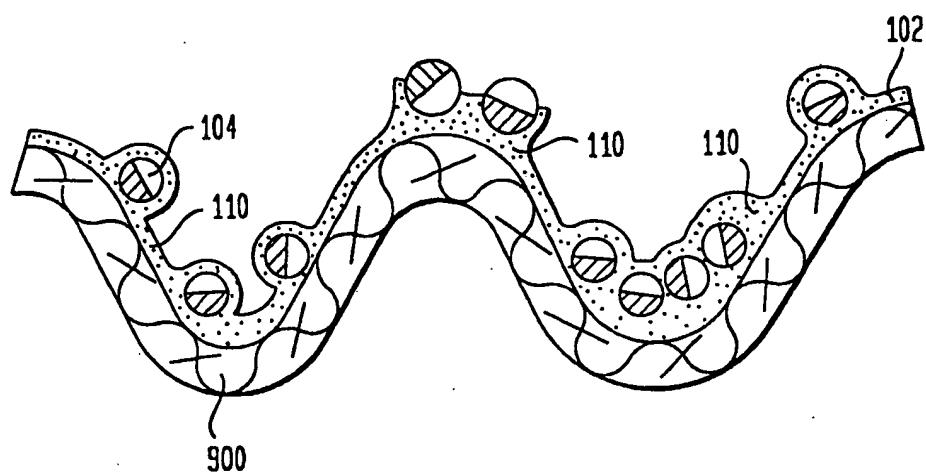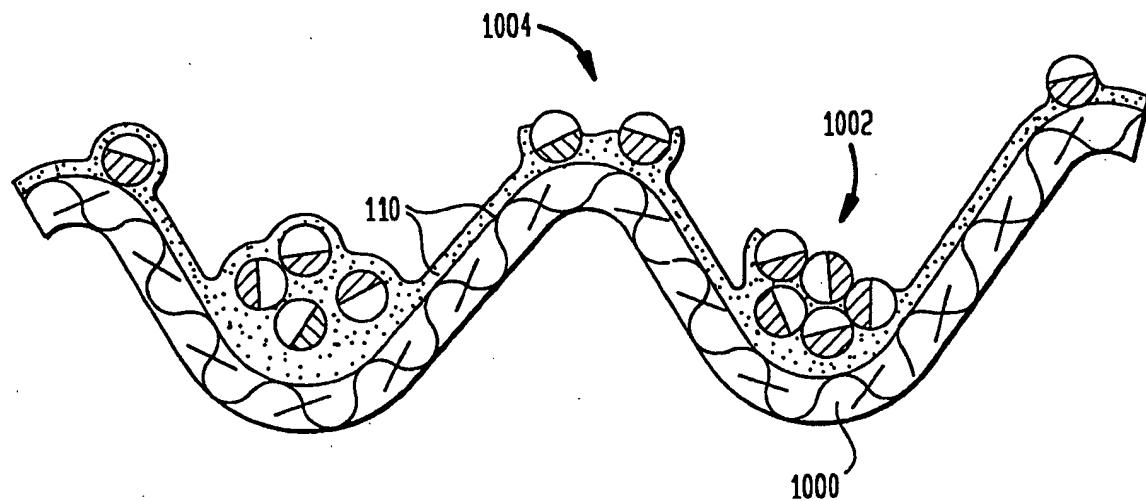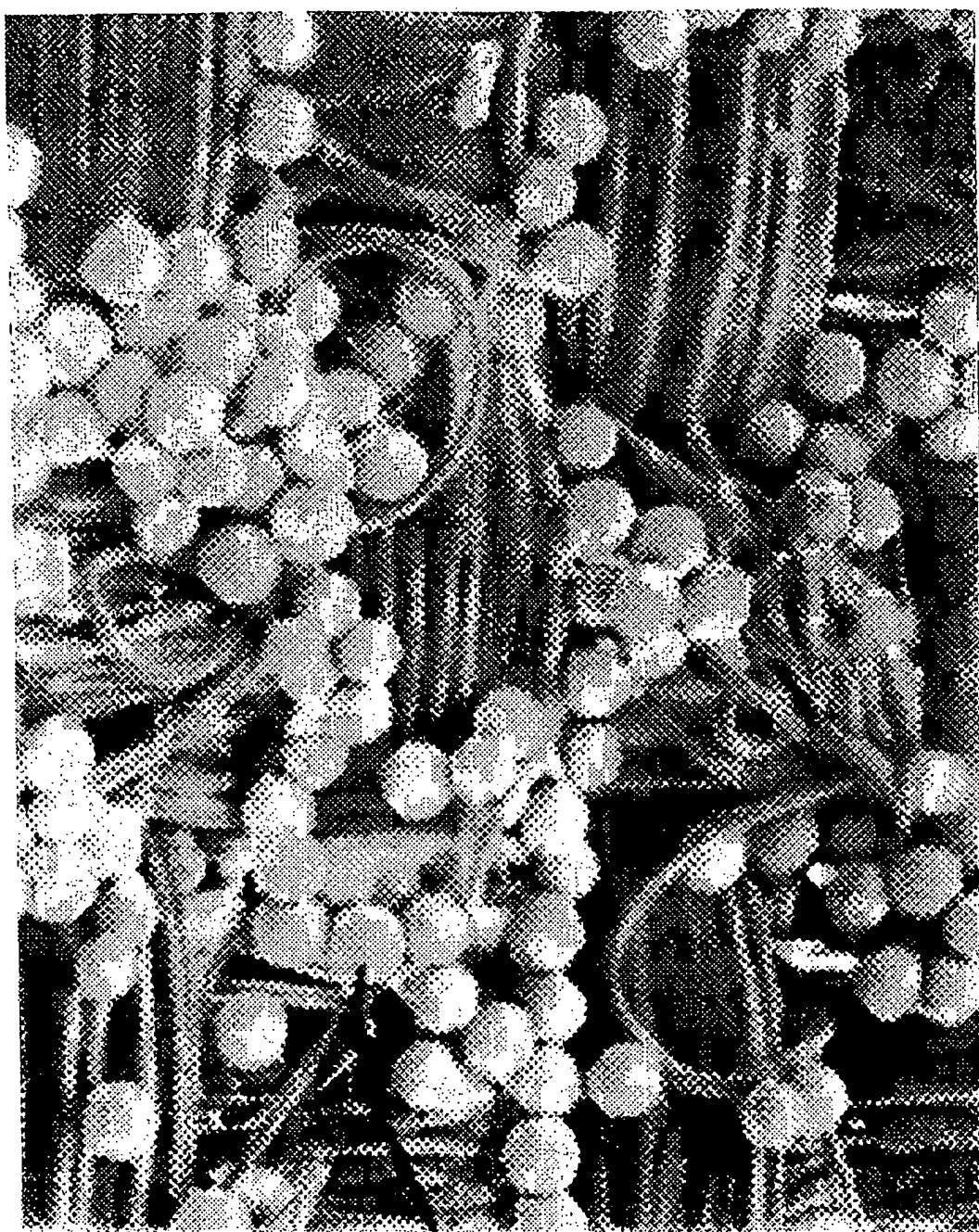
# EXAMPLE RETROREFLECTIVE COMPOSITION HAVING MBPVC RATIO OF 200%

Parts by Volume

		volatile	non volatile
1.	Water	49.1	
2.	Matrix Material Acrylic Copolymer (Hystretch V-29 100% solid from BF Goodrich)		30.49
3.	Dispersant to aid in suspending particles. Acrylic Polymer. (Alcosperse AD 40% solids from Hydrolabs)	0.43	0.12
4.	Thickener to maintain the proper viscosity. Acrylic Polymer (ASE-60 from Rhom & Haas)	.96	0.93
5.	Fixer to enhance cross-compositioning Methylated Melamine Formaldehyde (Aricel PC6A 79% solids from Astro Industries)	0.54	1.52
6.	Pigment particles with diameters averaging less than 2 microns Pigment cake, 100% solid		3.33
7.	Silane (Z-6040 Dow Corning)		0.67
8.	Hemispherically Reflective Dry AL Glass Beads of 1.9 refractive index averaging 50 microns		11.91
	Total	51.03	48.97

Fig.12

INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6   G02B5/128

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6   G02B   C09D   D06Q

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 96 17264 A (REFLECTIVE TECHNOLOGIES, INC) 6 June 1996 see the whole document ---	1-37
A	US 3 420 597 A (NELLESSEN ALFRED H ET AL) 7 January 1969 cited in the application see column 3, line 31 - column 9, line 13; figures 1-3 ---	1,4,7-9, 12-15, 18-21, 27,30, 33,36,37
A	EP 0 305 074 A (MINNESOTA MINING & MFG) 1 March 1989 see page 3, line 36 - page 7, line 48; figures 1,2 ---	1,8,10, 11,15, 20,23,33
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[X] Further documents are listed in the continuation of box C.   [X] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
14 October 1998	22/10/1998

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	THEOPISTOU, P

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	WO 97 10522 A (MINNESOTA MINING & MFG) 20 March 1997 see page 4, line 18 – page 6, line 10 see page 9, line 1 – page 10, line 28 see page 17, line 7 – line 22 see page 18, line 24 – page 21, line 10 ---	1-6, 8-17,20, 22,23, 28,30, 33-35
A	US 4 263 345 A (BINGHAM WALLACE K) 21 April 1981 cited in the application see column 3, line 28 – column 6, line 18; figure 1 ---	1,4, 8-15,18, 20,21, 23-27, 33,36
A	EP 0 389 114 A (MINNESOTA MINING & MFG) 26 September 1990 see page 4, line 9 – page 8, line 4; claim 4; figures 1-6 -----	1-37

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